

# An Experimental Comparison of Ammonia-Water and Ammonia-Water Lithium Bromide Mixtures in an Absorption Heat Pump

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## ABSTRACT

The performance of an absorption heat pump (AHP) operating with ammonia-water and ammonia-water-lithium bromide mixtures is compared. The AHP was designed for the ammonia-water system but operated successfully and without modifications with the ternary system. The pressures and most of the temperatures showed only minor differences. The COP of the AHP operating with a ternary mixture having a LiBr/H<sub>2</sub>O mass ratio of 0.48/0.52 was, on average, 0.05 lower than with the binary system. However, several factors indicated that the refrigerant vapor entering the rectifier had a significantly lower water content with the ternary system, as predicted in the literature.

## INTRODUCTION

Absorption heat pumps are based on the reversible absorption of a refrigerant by a second substance, the absorbent. The absorbent can be a liquid, solid, a mixture of a solid and liquid, or a solution of a solid and the refrigerant. Each type of refrigerant-absorbent system possesses advantages and disadvantages. Liquid absorbents tend to have good heat and mass transfer characteristics and are ideally suited to a continuous process. The liquid absorbent is volatile, so that the refrigerant vapor is not pure but contains absorbent as well. This generally necessitates a rectification process, requiring extra equipment and expenditure of energy, to purify the refrigerant vapor. Solid absorbents are nonvolatile, eliminating the need for rectification. The reaction between refrigerant and a solid absorbent goes nearly to completion at a constant temperature and pressure. Solid absorbents, however, are generally usable only in a discontinuous process and present problems of heat and mass exchange into a fixed absorbent bed. The use of a solid salt dissolved in a refrigerant to form an absorbent solution combines the ability to operate in a continuous process with the advantage of a nonvolatile absorbent. However, the heat and mass transfer characteristics of such a solution are often inferior to those of truly liquid absorbents and under some conditions the dissolved salt can crystallize out of solution.

To date, most refrigerant-absorbent combinations suggested or actually employed for use in AHPs have consisted of only two chemical species. It is possible that by combining two absorbents, the resulting mixture might retain the advantages but not possess the liabilities of the individual components (British Patent 1915, Unger 1957).

This work is concerned with the ternary mixture ammonia-water-lithium bromide (NH<sub>3</sub>-H<sub>2</sub>O-LiBr). The ammonia-water pair possesses very good thermodynamic and heat and mass transfer characteristics but requires rectification to remove water from the refrigerant vapor. Lithium bromide is a nonvolatile salt in the temperature ranges of interest here and is an absorber for ammonia as well as water. This ternary system has the advantage that, at least for pairs of the three components, the thermodynamic properties and materials' compatibility are well known.

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The thermodynamic properties of the  $\text{NH}_3\text{-H}_2\text{O-LiBr}$  system (principally for a  $\text{LiBr/H}_2\text{O}$  ratio of 60/40 weight percent) have been investigated (Radermacher et al. 1981, 1982). Upon adding lithium bromide to the  $\text{NH}_3\text{-H}_2\text{O}$  binary system, the most obvious effect is a lowering of vapor pressure. This is shown in Figures 1a and 1b comparing the vapor pressures of the binary and ternary mixtures as a function of temperature and fraction ammonia. (The composition in this figure is expressed on a salt-free molar basis; i.e., composition = moles  $\text{NH}_3$  / (moles  $\text{NH}_3$  + moles  $\text{H}_2\text{O}$ ). Since the lithium bromide is nonvolatile, this composition basis is useful for comparing the ternary system with the  $\text{NH}_3\text{-H}_2\text{O}$  binary system.) The overall width of the solution field is increased; the greater slope for the ternary system vapor pressure lines reflect a heat of vaporization that is higher by approximately 15%.

The dew and bubble lines at 294 psia (2 MPa) (which is typical of the high side pressure of a  $\text{NH}_3\text{-H}_2\text{O}$  AHP) for the two mixtures are shown in Figure 2. At a temperature of 365 F (180°C), the liquid mole fractions of ammonia are 0.15 for the binary and 0.35 for the ternary on a salt-free basis; the corresponding vapor compositions are 0.55 and 0.85 mole fraction ammonia respectively. Thus, for a given set of conditions in a generator, the ternary mixture allows a higher fraction of ammonia in the boiling absorbent solution, resulting in vapor with a lower water content, in this case, one-third of that for the binary system. The energy requirements and surface area for the rectification process would be reduced accordingly.

A major advantage of a ternary mixture in an absorption heat pump would be its increased refrigerant vapor purity. The attendant decrease in rectification requirements would allow a smaller rectifier (or in some applications none at all) to be used. The decreased heat of rectification would increase the COP of the cycle by 5% to 20% for the following reasons (Radermacher et al. 1981, 1982). In an AHP the weak absorbent flowing from the absorber to the generator can be preheated by heat exchange with three separate heat sources within the cycle: (1) heat exchange with the strong absorbent exiting the generator, (2) the heat of rectification, and (3) a portion of the absorber heat. At some point, the sum of these three possible heat flows exceeds the heat required by the weak absorbent stream. The surplus heat of one or more of these sources cannot be utilized for the production of refrigerant vapor in the generator. This surplus heat can contribute to the heating capacity, but at a COP of only unity since it cannot serve to increase the heat extracted from the low temperature source. With the ternary system, a greater fraction of these three heat flows can be utilized to preheat the weak absorbent, thus either reducing the high temperature heat requirement of the generator or increasing its vapor production rate.

A second advantage of the ternary mixture results from its wider solution field. Because of the greater temperature "overlap" between different processes in the cycle, more efficient advanced cycles employing extensive internal heat exchange may be feasible with a ternary mixture (Phillips 1984, Hayes 1984, Reimann 1984). Because of the fixed design of the current heat pump under test, this aspect will not be considered.

The addition of LiBr to the  $\text{NH}_3\text{-H}_2\text{O}$  system has other ramifications. The viscosity is increased, thus increasing pumping power requirements and reducing heat and mass transfer coefficients (Niebergall 1949). The possibility that these disadvantages might render the use of the ternary mixture infeasible is a concern. The sensible heat capacity of the ternary is roughly one-half that of the binary; this would reduce the losses associated with sensible heat exchange. Finally, because of the affinity of lithium bromide for ammonia, the solubility of LiBr in an ammonia-water solution is increased over that in pure water, thus reducing the risk of crystallization.

The objective of this work was to investigate the effects of adding lithium bromide to an existing absorption heat pump designed to operate with the ammonia-water system, thus avoiding the time and expense associated with the design of a new unit. The current tests are intended to determine whether the expected reduced heat and mass transfer rates and increased pumping requirements present a prohibitive restriction to the use of a ternary mixture with existing AHP technology and equipment. Since the heat pump was not designed for the ternary, comparisons of the overall performance of the  $\text{NH}_3\text{-H}_2\text{O}$  and  $\text{NH}_3\text{-H}_2\text{O-LiBr}$  systems are likely to be misleading, thus the emphasis is on examining differences in thermodynamic system states around the cycle.

#### HEAT PUMP DESCRIPTION

The absorption heat pump tested in this work was a prototype developed by an American manufacturer under government sponsorship. It is a gas-fired, heating-only, air-to-water heat pump and has been described by Kuhlenschmidt and Merrick (1983). The unit is sized for a

residential application and, except for the load heat exchanger and its associated circulating pump, is contained in a single cabinet, that is designed for outdoor operation.

The heat pump utilizes an ammonia-water absorption cycle, as shown in Figure 3. The generator is directly fired by natural gas. The absorbent streams entering and leaving the generator are heat exchanged and the refrigerant vapor purified in the analyzer and rectifier. The rectifier employs a triple heat exchanger, which preheats the incoming weak absorbent by heat exchange with the exiting strong absorbent in a concentric tube exchanger as shown in Figure 4. The weak absorbent is also heated by the partial condensation of an ammonia-water vapor mixture on the outside of the triple heat exchanger. Rectification also occurs on the inside of the rectifier shell, with the heat being lost to the surroundings.

A flue gas heat exchanger improves the burner efficiency by transferring heat from the combustion products to the strong absorbent stream, although at the expense of increasing the temperature and thus the vapor pressure of the absorbent entering the absorber. Weak absorbent from the falling-film type absorber is returned to the generator/rectifier by the positive displacement diaphragm-type solution pump.

In this particular unit, the heat of rectification and the heat provided by the strong absorbent coming from the generator are used to preheat the weak absorbent flowing to the generator. This design provides sufficient preheating capacity for the binary system. Therefore, the portion of the absorber heat that is at a suitable temperature for preheating purposes is given off to the cooling water, thus contributing to the heating capacity of the unit at a COP of only unity. The reduced heat of rectification expected with the ternary mixture may result in insufficient preheating of the weak absorbent solution because of the fixed design of the heat pump. (A portion of the absorber heat was not used in these experiments because of the major hardware changes involved.) Due to this mismatch, an increase in COP with the ternary cannot be expected.

An auxiliary electric heater was installed on the weak absorbent line at the outlet of the solution pump in an attempt to simulate the effects of preheating the weak absorbent with a portion of the absorber heat. This heater also reduced the effectiveness of the rectifier by increasing the temperature of the inlet weak absorbent stream and thus should result in a reduced refrigerant vapor purity. The heater consisted of nichrome wire in small ceramic tubes arranged around the outside of the tube carrying the weak absorbent. The ceramic tubes were potted in a silica compound and insulated with ceramic paper and fiberglass. The overall length of the heated section was 1.0 m. The total heat input to the weak absorbent was varied from 0 to 2.0 kW by a variable transformer.

#### EXPERIMENTAL PROCEDURE

The heat pump was tested in an environmental chamber with controlled dew-point and dry-bulb air temperatures. Water at a constant temperature and flow rate was pumped to the unit, where it flowed in parallel to the condenser and absorber. The installed instrumentation and test procedures are described by McLinden et al. (1983, 1984). The steady-state tests lasted for 30 minutes with average values of all measurements used for analysis. The tests followed, where applicable, the procedures outlined by Weber et al. (1984).

Sampling of the strong and weak absorbent solutions was done immediately after the conclusion of a steady-state test with the heat pump still operating. The sample lines were first purged and then solution was allowed to flow into preweighed flasks containing a known quantity of sulfuric acid. The flasks were reweighed to determine the quantity of sample and titrated to determine the amount of ammonia in the sample. To determine the quantity of LiBr, the titrated sample was heated to dryness at 176 F (80°C) to precipitate the nonvolatile components (principally as  $\text{Li}_2\text{SO}_4$  and  $\text{NH}_4\text{Br}$ ). The accuracy of the ammonia and LiBr mass fraction measurements are estimated to be 0.01 and 0.05 respectively. The composition of the circulating refrigerant was calculated by assuming that the vapor leaving the rectifier was saturated at the measured temperature and pressure.

The charge of the heat pump was adjusted with the machine operating at an ambient temperature of 32 F (0°C). The charge of solution was adjusted to a level in the analyzer specified by the manufacturer. The charge of ammonia was adjusted to obtain a 4 F (2°C) temperature rise between the evaporator inlet and outlet. This criterion corresponds to nearly complete vaporization of the refrigerant in the evaporator and is near the point of optimum COP at the charging temperature.

## RESULTS AND DISCUSSION

### The Binary System Ammonia-Water

For reference purposes the heat pump was tested before adding lithium bromide. The overall capacity and COP for the binary mixture were within 5% of the results obtained during a series of tests conducted 18 months previously. These results indicate that the heat pump and instrumentation were not significantly affected by the lengthy periods of nonoperation or the tests conducted between 1982 and 1984. The small differences between the two series of tests would be consistent with a slightly higher charge of ammonia compared with that for the earlier tests.

### Comparison of the Binary and Ternary Mixtures

The absorption heat pump did not exhibit any operational problems with the ternary system. In particular, there were no prohibitive or obvious restrictions to heat or mass transfer, and the system temperatures and pressures were in the same range as for the binary system.

The heat pump was tested at ambient temperatures of 17 F (-8°C) and 47 F (8°C) with two compositions of the ternary (LiBr/H<sub>2</sub>O mass ratios of 0.38/0.62 and 0.48/0.52) in addition to the baseline tests with the NH<sub>3</sub>-H<sub>2</sub>O system. For each combination of absorbent mixture and ambient temperature, tests were run with the auxiliary heater at 0 and 2.0 kW.

In comparing the test results for the different absorbent mixtures (Table 1), the addition of the higher concentration of lithium bromide to the system decreased the COP by an average of 0.05. Because the generator heat input was fixed, the heating capacity followed the same trends as COP. Somewhat surprisingly, most of the system temperatures showed only minor differences of 2-4 F (1 - 2°C) between the different mixtures. The mass fractions of ammonia in the strong and weak absorbent solutions were lower with the ternary mixtures; however, the molar ratio of NH<sub>3</sub> to H<sub>2</sub>O was significantly higher.

The composition of the refrigerant at the rectifier outlet was virtually identical for the three absorbent mixtures. This result is in contrast to the above arguments which predicted a lower water content in the refrigerant vapor for the ternary system. This result is due to the fact that the rectifier was oversized for this application, so that the composition of the (saturated) vapor stream was determined by its temperature and pressure at the rectifier outlet rather than the vapor composition at the rectifier inlet. The temperature of the outlet vapor is determined, in turn, largely by the temperatures of the weak and strong absorbent streams at the end of the rectifier. Since the refrigerant composition and the measured high and low side pressures were similar, the refrigerant side of the cycle (i.e., the condenser and evaporator) was also unaffected by the absorbent mixture.

Although the water content of the refrigerant vapor exiting the rectifier is unchanged for the different absorbent systems, three factors indicate that the vapor entering the rectifier from the generator/analyzer has a lower water content for the ternary system. An indication of the relative heat transfer coefficients for the different mixtures is provided by a thermocouple embedded in the potting compound of the auxiliary heater. The ratio of the heater power to the temperature difference between the heater and the solution flowing inside is proportional to the overall heat transfer coefficient. However, since the quantity  $(\dot{Q}/\Delta T)_{\text{heater}}$  includes the constant but unknown resistance of the potting material and tube wall, the film coefficient for the absorbent solution cannot be separately determined. Because of the higher viscosity of the ternary, the overall heat transfer coefficient decreased with increasing lithium bromide content. The lower heat transfer coefficients for the ternary mixture inside the triple heat exchanger would decrease the effectiveness of the rectifier simultaneously with the decreased need for rectification.

The temperature driving force to condense the vapor in the rectifier is provided by the inlet weak absorbent stream. With the ternary system, the temperature of the weak absorbent stream was higher by approximately 7°F (4°C), resulting in a second factor which would reduce the rectification effectiveness.

Finally, the rectifier shell temperature is lower by an average of 7 F (4°C) for the ternary mixture. This indicates that less rectification is occurring on the shell. The temperature change of the rectifier shell is more distinct, 9 F (5°C), at the lower outdoor temperature, indicating that the effect of the lithium bromide is stronger when the need for rectification increases, as predicted in the literature. Previous tests with an increased ammonia charge and thus higher ammonia compositions in the binary system (McLinden 1984)

revealed a similar drop in rectifier shell temperature. Each of the above three factors indicate a reduced rectifier effectiveness with the ternary working fluid. Since the outlet water vapor content was unchanged, the inlet water vapor content is less for the ternary. These results suggest that the rectifier was oversized for the ternary system.

The input of 2.0 kW of heat to the weak absorbent stream with the auxiliary heater had a number of consequences as indicated in Table 1. The most direct effect was to increase the temperature of the weak absorbent flowing to the rectifier; this reduced the temperature driving force for rectification as discussed above and resulted in a lower refrigerant vapor purity. The temperature of the strong absorbent was also increased; the higher absorber temperature led to a higher low side pressure. Because less of the generator heat input was required to bring the incoming weak absorbent to boiling, the refrigerant mass flow rate was increased when the auxiliary heater was on. These effects are similar for the binary and ternary fluid systems.

These changes in system states had competing effects on COP and capacity and thus the overall effect of the auxiliary heater varied for the different ambient temperatures and fluid mixtures. The higher refrigerant flow rate would permit a greater heat flow from ambient which would increase COP and capacity. The higher absorber and evaporator pressure would increase the saturation temperature of the refrigerant and thus reduce the temperature difference for heat exchange in the evaporator. The higher refrigerant water content would require lower evaporator pressures for complete vaporization. For the lower ambient temperature, the increase in capacity with the heater is less than the 2.0 kW heater input and the COP decreases. (At this ambient condition the evaporator cannot vaporize the entire refrigerant flow (McLinden 1984)). At the higher ambient temperature, the COP improved with the heater for the binary mixture but was unchanged for the ternary. While the auxiliary heater simulated many of the effects of preheating the weak absorbent with absorber heat, the remainder of the cycle was not optimized for this additional heat flow and thus no conclusions can be drawn about the benefits of such an arrangement for either the binary or ternary fluid systems.

The refrigerant and weak absorbent mass flow rates were calculated using the stream compositions, heat flows, an energy balance around the condenser, and a mass balance around the absorber (as described by McLinden (1983)). Increasing the heater power from zero to 2.0 kW increased the refrigerant mass flow rate by an average of 6%. In going from the binary mixture to the ternary with the higher LiBr content, the refrigerant flow decreased by 4%, which is consistent with the higher heat of vaporization predicted for the ternary. The mass flow rate through the solution pump (weak absorbent) was 12% higher for the ternary. This latter result suggests that in the solution pump the higher density for the ternary offsets the higher viscosity. The electric input to the heat pump (including the fan and controls) changed by less than 1% for the three absorbent mixtures, indicating that the pumping power requirements were virtually unchanged.

## CONCLUSIONS

An absorption heat pump designed for the ammonia-water system was operated successfully and without difficulties with the ternary system  $\text{NH}_3\text{-H}_2\text{O-LiBr}$ . The COP of the heat pump was, on average, 0.05 lower with the ternary mixture. There were only minor differences in the system pressures, pumping power requirements, and most of the temperatures between the binary and ternary systems. The purity of the refrigerant vapor leaving the rectifier was unchanged for the different absorbents due to the rectifier configuration. However, several factors, including a lower rectifier shell temperature and reduced temperature driving forces in the rectifier, indicated that the vapor entering the rectifier from the generator/analyzer had a lower water content with the ternary system. The overall conclusion of this work is that the ternary system does not impose any prohibitive restrictions to its use and that the construction of a prototype absorption heat pump specifically designed for the ternary is worthwhile.

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TABLE 1  
Summary of Test Results for the NH<sub>3</sub>-H<sub>2</sub>O System and Two NH<sub>3</sub>-H<sub>2</sub>O-LiBr Mixtures  
at Two Ambient Temperatures and two Auxiliary Heater Power Inputs

Mixture	NH <sub>3</sub> -H <sub>2</sub> O		NH <sub>3</sub> -H <sub>2</sub> O-LiBr #1 LiBr/H <sub>2</sub> O ratio = 0.38/0.62		NH <sub>3</sub> -H <sub>2</sub> O-LiBr #2 LiBr/H <sub>2</sub> O ratio = 0.48/0.52		NH <sub>3</sub> -H <sub>2</sub> O		NH <sub>3</sub> -H <sub>2</sub> O-LiBr #1 LiBr/H <sub>2</sub> O ratio = 0.38/0.62		NH <sub>3</sub> -H <sub>2</sub> O-LiBr #2 LiBr/H <sub>2</sub> O ratio = 0.48/0.52	
Heater Power (kW)	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0	0.0	2.0
Ambient temp (°C)	-8.5	-8.2	-8.4	-8.2	-8.2	-8.2	8.5	8.8	8.3	8.0	8.1	8.4
Load water temp (°C)	40.7	40.6	40.8	40.6	40.6	40.6	40.7	40.7	40.6	40.6	40.3	40.6
COP	1.01	0.98	0.97	0.93	0.97	0.94	1.11	1.13	1.08	1.08	1.06	1.07
Heating capacity (kW)	14.7	16.3	14.1	15.5	14.2	15.6	15.8	18.2	15.4	17.4	15.3	17.3
Mass fraction NH <sub>3</sub>	0.113	0.115	0.100	0.100	0.111	0.111	0.166	0.158	0.132	0.129	0.140	0.138
strong absorbent	0.296	0.299	0.256	0.263	0.263	0.267	0.345	0.346	0.298	0.302	0.302	0.304
weak absorbent	0.992	0.983	0.993	0.983	0.993	0.983	0.994	0.986	0.994	0.984	0.994	0.984
refrigerant												
Salt-free mol frac NH <sub>3</sub>	0.119	0.121	0.159	0.159	0.203	0.203	0.174	0.166	0.206	0.202	0.249	0.246
strong absorbent	0.308	0.311	0.370	0.378	0.421	0.426	0.358	0.359	0.420	0.425	0.468	0.470
weak absorbent	0.992	0.984	0.993	0.984	0.993	0.984	0.994	0.987	0.994	0.985	0.994	0.985
refrigerant												
Pressures (MPa)												
absorber	0.241	0.245	0.243	0.255	0.251	0.256	0.341	0.364	0.346	0.372	0.358	0.382
rectifier	2.27	2.34	2.24	2.29	2.25	2.29	2.37	2.45	2.31	2.38	2.32	2.37
(Q/ΔT) heater (W/°C)	-	27.9	-	23.1	-	19.5	-	27.3	-	23.3	-	20.3
Temperatures (°C)												
rectifier shell	124.8	130.2	120.5	125.8	119.4	125.4	115.2	122.0	114.9	120.1	112.8	120.1
rect vapor outlet	78.9	91.3	76.0	90.9	76.4	90.1	75.6	88.9	74.6	90.2	74.5	90.2
rect weak abs in	45.2	63.7	45.7	69.1	49.7	71.4	48.6	68.1	50.2	73.8	52.4	76.4
rect strong abs out	62.7	76.4	64.3	81.5	67.6	83.7	63.1	77.9	65.1	83.5	67.4	85.8
Mass flow rates (kg/s)												
refrigerant	.0050	.0053	.0047	.0050	.0048	.0051	.0053	.0057	.0050	.0053	.0051	.0054
weak absorbent	.024	.025	.027	.026	.028	.029	.025	.025	.026	.026	.027	.027

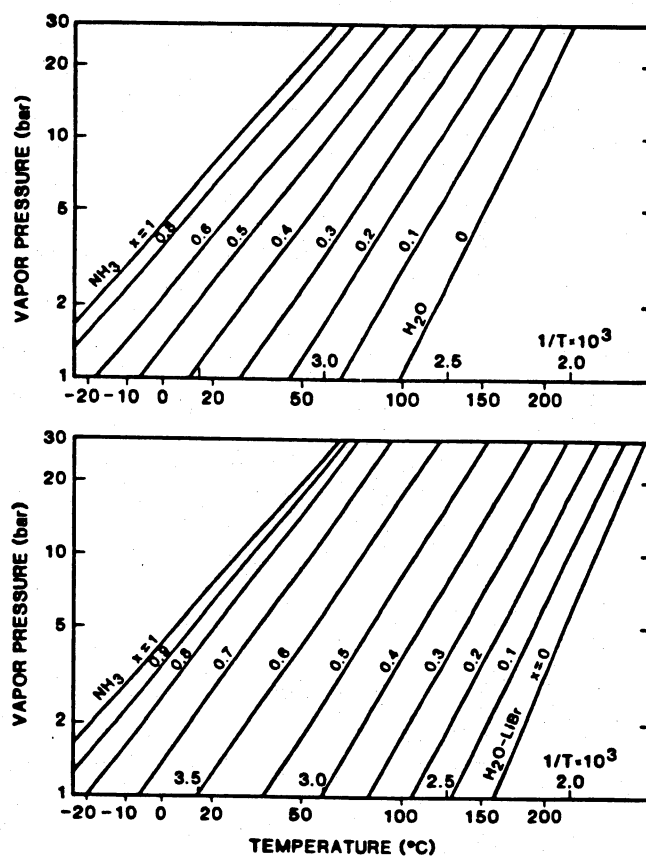


Figure 1. Comparison of equilibrium vapor pressures as a function of temperature and mole fraction ammonia for the binary and ternary systems (adapted from reference four)

- $\text{NH}_3\text{-H}_2\text{O}$  system
- $\text{NH}_3\text{-H}_2\text{O-LiBr}$  system with a  $\text{LiBr/H}_2\text{O}$  ratio of 60/40 mass percent (compositions given on a salt-free molar basis)

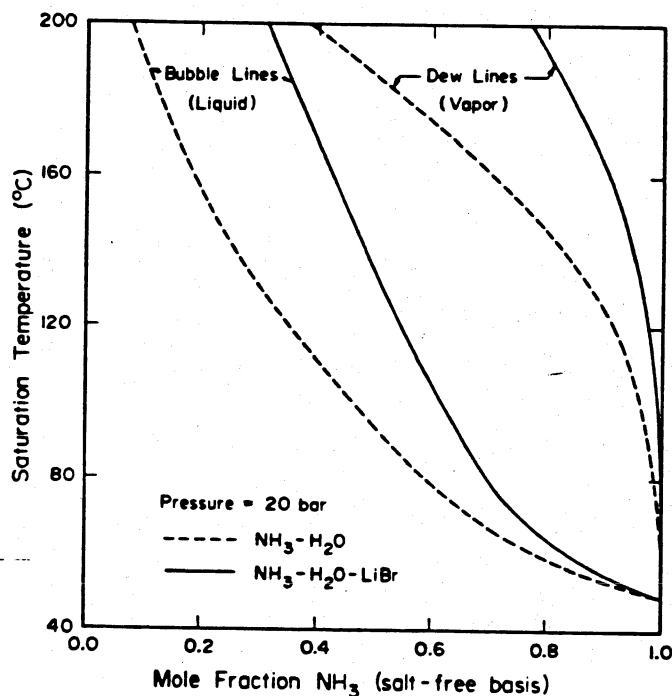


Figure 2. Comparison of bubble and dew lines at 20 bar for the  $\text{NH}_3\text{-H}_2\text{O}$  system and the  $\text{NH}_3\text{-H}_2\text{O-LiBr}$  ternary system with a  $\text{LiBr/H}_2\text{O}$  ratio of 60/40 mass percent (adapted from reference four)



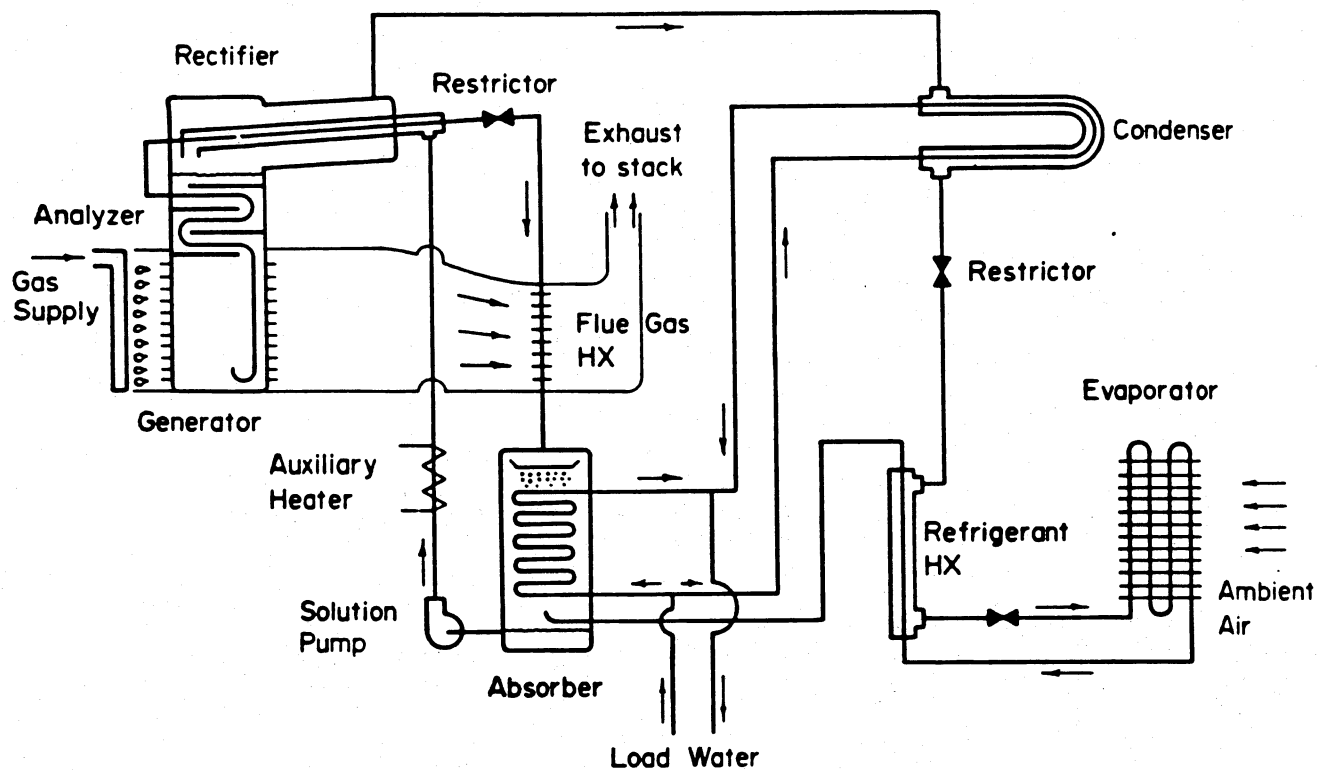


Figure 3. Schematic of the absorption heat pump

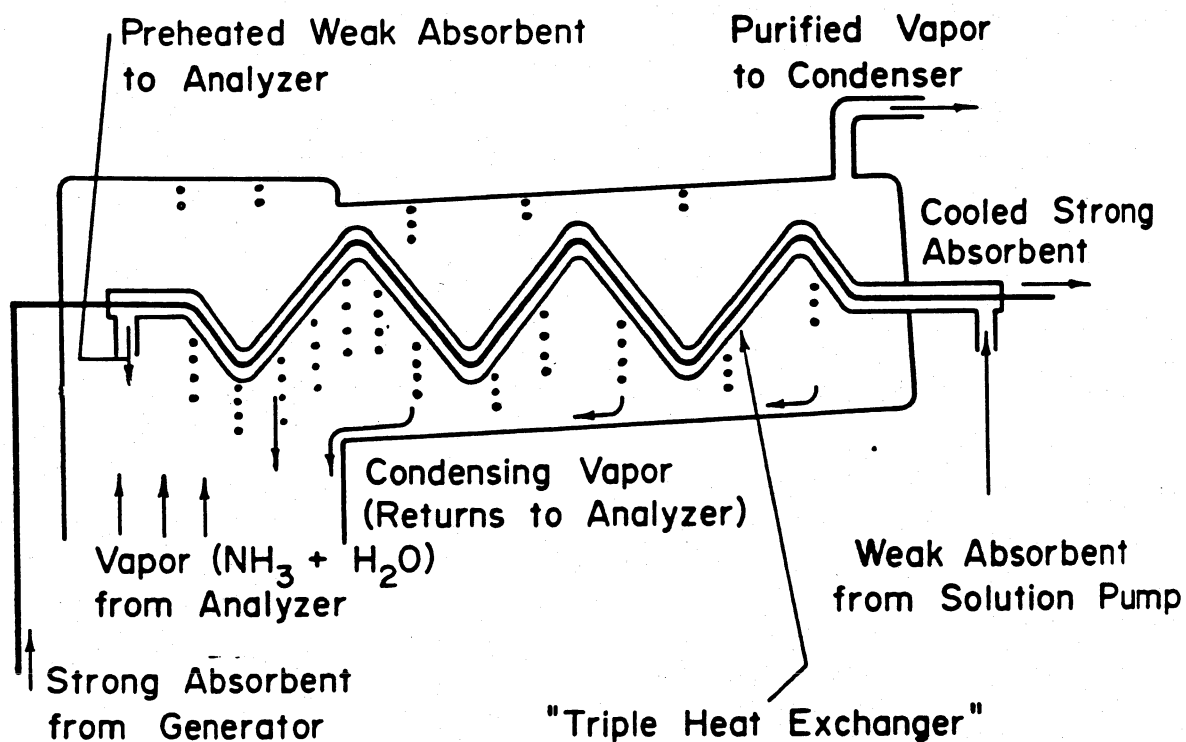


Figure 4. Detail of flows in the rectifier of the AHP

## Discussion

D.K. MILLER, Borg Warner Air Conditioning, Inc., York, PA: What efforts were exerted to control skin temperature (what were the temperatures)? What inhibitors and what metals were used?

RADERMACHER: The skin temperature has not been measured, since this would have required cutting into a sealed system. The metals used were those that are commonly employed in ammonia/water absorption systems, and the only corrosion inhibitor supplied was the one contained in the commercially obtained salt solution. The goal of this experiment was not to determine heat transfer and corrosion properties, rather than prove that the ternary fluid mixtures perform according to expectations in existing machinery.

H. PEREZ-BLANCO, Oak Ridge (TN) National Laboratory:  $\text{NH}_3\text{-H}_2\text{O-LiBr}$ : It does not appear that the corrosion behavior of this mixture with austenitic steel is too severe after a passivation phenomena which occurs naturally.

RADERMACHER: Our own corrosion tests, although somewhat limited, due to a lack of specific equipment, showed as well as those performed by interested manufacturers that corrosion does not seem to be a severe problem in the temperature range of interest.